



(12) UK Patent (19) GB (11) 2 187 466 (13) B

(54) Title of Invention

Anticorrosive material

(51) INT CL⁴: C08L 23/06, C08K 9/00, C09D 5/08

(21) Application No
8700299.4

(22) Date of filing
23 May 1985

(43) Date of printing by UK Office
9 Sep 1987

(45) Patent published
13 Sep 1989

(86) International application data
PCT/SU85/00040
Su 23 May 1985

(87) International publication data
WO86/07077
Su 4 Dec 1986

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(52) Domestic classification
(Edition J)
C3V VDP VEF VEK
C3W W217
U1S S3010

(56) Documents cited
SU 000761537 A
SU 000566458 A

(58) Field of search

As for published application
2187466 A viz:
INT CL⁴ C08L 23/06,
C08K 9/00, C09D 5/08
updated as appropriate

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ANTICORROSIVE MATERIAL

The present invention relates to the production of agents for corrosion protection of metals combining barrier properties of polymers with the ability of corrosion inhibitors to chemically suppress the corrosion process; more particularly, this invention relates to anticorrosive materials. These materials can be used for the manufacture of sealing construction members (gaskets, sealing rings and washers and the like), striping anticorrosive coatings, as well as for the manufacture of film-like materials and anticorrosive packing aids employed for corrosion proofing and packing of metal articles.

Polymeric films and coatings with a thickness of up to several millimeters are not an impermeable barrier for diffusion of water, oxygen, electrolytes. Protective properties can be substantially enhanced by introducing corrosion inhibitors into polymeric compositions.

Anticorrosive materials for films and coatings based on cellulose esters, polyacetals, polyesters have been produced by mixing polymer solutions or powders with corrosion inhibitors compatible with the polymeric base, followed by a heat-treatment. For example, known in the art is an anticorrosive material incorporating, as a corrosion inhibitor, a mixture of an amine nitrate and an ammonium salt of an aliphatic carboxylic acid (cf. US Patent No. 3,462,329 Cl. 156-190, issued in 1969).

A disadvantage of these anticorrosive materials resides in a high cost of the polymeric base, as well as a limited range of articles being protected from corrosion.

Known in the art are packing anticorrosive materials produced by extrusion of a mixture of polyethylene or another chemically resistant polyolefine with heat-resistant corrosion inhibitors comprising a mixture

of inorganic salts; α -dicyclohexylamine, β -cyclohexylammonium nitrite, nitrosocyclohexylamine (cf. Japanese Patent No. 49-21223, Cl. 12 A 82, published in 1974).

A disadvantage of these prior art packing materials resides in a low level of protective properties due to volatilization of the inhibitor during manufacture of these materials and due to an irreversible retention of a portion of the introduced inhibitor in the polymeric film.

Anticorrosive properties of inhibited polymeric materials are defined by the effectiveness of migration of the inhibitor towards the surface of the material to be protected.

The present invention aims to provide an anticorrosive material with controllable and timestabilized supply of corrosion inhibitors towards the surface of the article being protected or into a cavity of a sealed packing and, hence, to improve effectiveness of utilization of corrosion inhibitors and enhance the effect produced by the anticorrosive protection.

The present provides an anticorrosive material comprising polyethylene plasticized with a mineral oil and containing as an oil-soluble corrosion inhibitor:

- (a) contact corrosion inhibitor selected from:
a sulphonated or nitrated mineral oil, or a product

of neutralization of a sulphonated or a nitrated mineral oil with an alkali, or a product of neutralization of a sulphonated mineral oil with urea, or bottoms from distillation of synthetic or naturally occurring fatty acids, or products of condensation of said bottoms with organic amines, or a product of condensation of an alkenylsuccinic anhydride and urea, or

(b) a volatile corrosion inhibitor selected from:
a salt of dicyclohexylamine and an organic acid, or tertiary amine having a nitrile group; or

(c) a mixture of both contact (a) and volatile (b) corrosion inhibitors,
the proportions of the anticorrosive material components being as follows, per cent by weight:

mineral oil	20-45
oil-soluble corrosion	
inhibitor	2-50
polyethylene	the balance.

The said alkali is suitably calcium hydroxide.

The anticorrosive material of the above-specified composition has a number of advantages, the principal of which resides in the possibility of a controlled and time-stabilized evolution of the corrosion inhibitor towards the surface of the protected articles or into a

sealed packing cavity, thus ensuring a high effectiveness of the anticorrosion protection [the rate of steel corrosion under a film or coating of this anticorrosive material in a neutral medium does not exceed 10^{-4} g/(m²h)]. Furthermore, the anticorrosive material according to the present invention has a wide range of physico-mechanical properties, a good processibility into articles. Thus, the material according to the present invention can be useful in the manufacture of parts of sealing units ensuring inhibition of a local corrosion of metal parts in these sealing units; a packing film protecting metal parts from atmospheric corrosion during transportation and storage; anticorrosive agents (vehicles for volatile corrosion inhibitors) to be placed inside a sealed packing.

The base of the anticorrosive material according to the present invention is comprised by a system "poly-ethylene - aliquid hydrocarbon plasticizer" in a gel-like state. A mixture of these components with an oil-soluble inhibitor is converted into a homogeneous solution upon heating to a temperature within the range of from 115 to 230°C (the temperature range is defined

by melting point and by the starting temperature of a thermo-oxidizing destruction of polyethylene). In the course of a subsequent cooling to a temperature of from 90 to 150°C its amorphous stratification occurs which, due to a high viscosity of the solution, is not accompanied by a complete separation of phases. Being localized in microregions comparable in size with supermolecular formations of polyethylene, the phase separation results in forming a polymeric matrix with a system of pores filled with a liquid low-molecular filler (a solution of the inhibitor in a mineral oil). This spontaneous separation of the liquid phase due to the occurrence of a relaxation processes in the material is called syneresis.

The pore size of the polymeric matrix is defined by the composition of the anticorrosive material according to the present invention and the time of residence at the amorphous stratification temperature and is equal to 10-30 μ m. An obligatory condition of transfer, in the mechanism of syneresis, of the inhibitor dissolved in the plasticizer towards the surface of the article to be protected is the availability of a system of communicating pores in the anticorrosive material. For a contact corrosion inhibitor syneresis is the only mode of supplying the inhibitor towards the surface of the protected article, while a volatile inhibitor is additionally transferred by way of migration and diffusion within the polymeric matrix.

The formation of communicating pores lowers maximum values of mechanical strength and deformability of the materials. However, physico-mechanical characteristics of a plasticized polyethylene filled with a corrosion inhibitor remain satisfactory for its use as a sealing construction and pecking material at a content of polyethylene above 50%.

An optimum combination of physico-mechanical and

anticorrosion properties of the material according to the present invention defines the upper and lower limits of concentration of the components.

For a plasticizing agent the lower limit (20% by weight) is defined by the condition of the process of syneresis, whereas the upper limit (45% by weight) - by the condition of satisfactory physico-mechanical properties of the anticorrosive material (e.g., for a packing material the tensile strength should not be less than 10 MPa, relative elongation - not less than 400%).

For an oil-soluble inhibitor the lower (2% by weight) and the upper (50% by weight) limits are defined by the condition of ensuring a required protecting concentration of the inhibitor on the metal surface, by the inhibitor effectiveness, as well as by efficiency of its supply towards the surface being protected. Furthermore, the upper limit for the inhibitor is defined by conditions of economic efficiency and the necessity of maintaining satisfactory physico-mechanical properties of the material.

The anticorrosion material according to the present invention is produced in the following manner. An oil-soluble corrosion inhibitor is mixed with a plasticizing agent (mineral oil) till the inhibitor is completely dissolved in the plasticizing agent. The resulting solution is mixed with a granulated polyethylene in a mixer of any type, for example in a drum mixer. The thus-produced composition is processed into an anticorrosive material by melting thereof and a subsequent extrusion, or injection moulding, or application of a coating from a melt by dipping. The method of injection moulding is used for the manufacture of sealing construction articles, the extrusion method - for the manufacture of an inhibited film.

A low-density ($\rho = 900-939 \text{ kg/m}^3$) or a high-density

($\rho = 949-959 \text{ kg/m}^3$) polyethylene is used for the production of the anticorrosive material according to the present invention.

As a plasticizing agent for polyethylene it is advisable to use, for example, the following mineral oils denoted by letters (a), (b) and (c):

(a) - a selective-purification mineral oil without additives produced from low-sulphur paraffin or low-paraffin crudes with the following basic characteristics: density at 20°C 0.89 g/cm^3 ; viscosity at 20°C - 14 cSt; ash content - at most 0.003%, acid number - 0.25 mg KOH/g; congelation temperature - $(-30)^\circ\text{C}$; closed-cup flash point - 200°C ;

(b) - a selective-purification mineral oil without additives produced from low-sulphur crudes with the following basic characteristics: density at 20°C - 0.897 g/cm^3 ; viscosity at 20°C - 20.5 cSt; ash content - at most 0.003%; acid number - 0.03 mg KOH/g, congelation point - $(-18)^\circ\text{C}$, closed-cup flash point - 250°C ;

(c) - distillate mineral oil of a high degree of purification with the following basic characteristics: density at 20°C - 0.894 g/cm^3 ; viscosity at 20°C - 49 cSt; at 50°C - 20 cSt; congelation point - $(-45)^\circ\text{C}$, open-cup flash point - 163°C .

Among contact-type oil-soluble inhibitors based on a sulphonated or nitrated mineral oil are effective, for the purpose of the present invention, oils denoted by letters A, B, C and D:

A - selective-purification nitrated mineral oil thickened by paraffin (10% by weight) which comprises a dark-brown oily liquid with the density of 0.96 g/cm^3 at 20°C , viscosity of 100 cSt at 20°C and 30 cSt at 100°C , ash content of 3.5%; it is soluble in mineral oils and organic solvents;

B - an oil solution of a mixture of calcium sulphonate and oxidized petrolatum; viscosity at 100°C - 32-40 cSt; acid

number - 0.04 mg KOH/g; ash content - 9%; it is soluble in mineral oils and organic solvents;

C - sodium sulphonate produced by neutralization of sulphonic acids contained in a sulphonated oil distillate with caustic soda; density at 20°C - 0.961 g/cm³,
5 viscosity at 100° C - 230 cSt; acid number - 0.04 mg KOH/g, ash content - 9%;

D - nitrated mineral oil neutralized with calcium hydroxide thickened with sterain (10% by weight) which
10 comprises a black oily liquid with the viscosity of 100 cSt at 100°C, density of 0.96 cm³/g at 20°C, ash content of 4.6%; it is soluble in mineral oils and organic solvents.

Among contact-type oil-soluble inhibitors based on bottoms of distillation of synthetic or naturally-occurring
15 fatty acids it is advisable to use, e.g., the following ones denoted by letters E and F;

E - salt of cyclohexylamine and synthetic fatty acids with 7 to 11 carbon atoms in a chain ($C_nH_{2n+1}COOH \cdot C_6H_{11}NH_2$);
20 this salt comprises a light-brown paste-like substance with the congelation point of -12°C soluble in alcohols, mineral oils, gasoline and acetone;

F - bottoms resulting from distillation of fatty acids of soapstock from crude cotton-seed oil and bone
25 fat; it consists mainly of high-molecular saturated and unsaturated fatty acids and contains a certain amount of unsplit fats and products of oxidation of fats and fatty acids; prevailing are compounds with C₁₀-C₂₄ chains; density of the bottoms is 0.90-0.95 g/cm³ at 20°C; viscosity
30 -65-70 cSt at 50°C; acid number 62 mg KOH/g; open-cup flash point - 260°C.

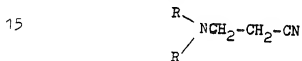
An effective contact-type corrosion inhibitor is also a product of condensation of an alkenylsuccinic anhydride and urea (denoted by letter G). It comprises
35 a light-brown liquid with the density of 0.89 g/cm³ at 20°C, viscosity of 25 cSt at 50°C, soluble in mineral

oils and organic solvents.

Among volatile oil-soluble corrosion inhibitors are effective, for example, the following denoted by letters H, I:

5 H - salt of dicyclohexylamine (at least 43% by weight) and a technical fraction of synthetic fatty acids with a number of carbon atoms of 10-20 in a chain; this salt comprises a paste-like product with a density of 0.91-
10 -0.93 g/cm³ at 20°C; melting point 15-20°C, soluble in mineral oils, organic solvents; volatility at 20°C - -0.013 Pa;

I - yellow to light-brown liquid based on a commercial fraction of secondary amines of fatty acids and acrylic acid nitrile; this product has a general formula:



wherein R is C_nH_{2n+1}, n = 7-9; density at 20°C - 0.85 g/cm³; viscosity at 40°C - 6 cSt; congelation temperature - (-40)°C; boiling temperature under the pressure of 1.33 kPa - 190°C; self-inflamma-
20 tion temperature - 260°C; soluble in mineral oils, alcohols, organic solvents, water; volatility at 20°C - 13.3 Pa.

For the production of the anticorrosive material useful for corrosion proofing and packing of metal artic-
les it is advisable to use a mixture of both contact and
25 volatile corrosion inhibitors.

For a better understanding of the present invention the following specific examples of particular composi-
tions are given hereinbelow in comparison with the anticorrosive material according to Japanese Patent
30 No. 49-21223.

Table 1

Component	Compositions of the anticorrosive material, by weight														Japanese Patent No 49-21223	
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV		
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Low-density polyethylene																
High-density polyethylene					50	65	53	58		50	53	20	30		30	50
Mineral oil:		45	55	65					58					30		
(a)		45	37	29					20			30				
(b)					41			27				30		20		
(c)						25	45						30		20	
Contact corrosion inhibitors:																
A			8									20			10	
B		10														
C				6												
D					9											
E						6										
F											15					
G										20						
Volatile corrosion inhibitors:							2	12	22				10			
H								3								
I						4									40	
Mixture of α -dicyclohexylamide, β -cyclohexylmethylamine nitrite and nitrosocyc-											2	30	40	50		

Table 1 (cont.)

Component Compositions of the anticorrosive material,
by weight

	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV	Japanese Patent No. 49-21223	
5																
10	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
	lobexyl-amine in mass ratio of 1:1:1															50

Properties of compositions 1-XIV of the anticorrosive material according to the present invention and those of the anticorrosion material according to Japanese Patent No. 49-21223 are shown in Table 2 hereinbelow.

The breaking tensile strength and relative elongation at rupture was determined by means of a breaking machine at the deformation speed of the moving clamp of 50 mm/min.

Corrosion tests were performed by the express-method through measurement of polarization resistance R_p of a bielectrode sensor contacting with a specimen of the test material in an electrolyte. Electrodes are used which are made of a carbon steel with a content of carbon of 0.09-0.15% by weight. The working surfaces of the electrodes were ground to the roughness of $R_a=0.4-0.5 \mu m$; non-working surfaces were insulated by paraffin. As the electrolyte a 1N solution of Na_2SO_4 was used. The rate of corrosion $[i, g/(m^2 h)]$ was determined by the formula:

$$i = \frac{2K_w}{S R_p}$$

wherein K_w - weight coefficient of corrosion depending on the type and concentration of the electrolyte, Ohm g/h (in a 1N solution of Na_2SO_4 $K_w = 0.032$);

R_p - polarization resistance, Ohm;
 S - area of mutual overlapping of the electrodes, m^2 (cf. "Protection of Metals", No.6, published in 1982, "Nauka" Publishers, Moscow; V.A.Goldadze, Ya.M.Zolotovitsky, A.S.Neverov, L.S.Pinchuk "Assessment of a Protective Ability of Inhibited Materials by the Method of Polarization Resistance", pp.946-949).

Table 2

	Composition No	Breaking tensile strength, MPa	Relative elongation at rupture, %	Rate of corrosion of a steel electrode contacting with the anticorrosive material film, $10^{-3} \text{ g}(m^2 \text{ h})$
10	I	13.0	-	0.17
	II	14.2	-	0.28
	III	17.1	-	0.05
20	IV	12.3	400	0.15
	V	15.4	480	0.3
	VI	12.8	550	0.6
	VII	13.2	450	0.5
	VIII	14.4	-	0.25
25	IX	11.1	-	0.31
	X	12.2	-	0.44
	XI	2.1	-	0.15
	XIII	3.5	-	0.11
	XIII	3.3	-	0.2
30	XIV	3.7	-	0.25
	Japanese Patent No. 49-21223	5.8	-	7.4

As it is seen from Table 2, by varying compositions, it is possible to control, within a wide range, physico-mechanical properties of the anticorrosive material.

The breaking tensile strength of the material according to the present invention is varied from values close to that of polyethylene (compositions I-X) to values characteristic for solid lubricants (compositions XI-XIV).
5 Relative elongation at rupture was measured for compositions IV-VII on the basis of low-density polyethylene advisable for the production of an inhibited film. This characteristic (400-550%) corresponds to the requirements imposed on proofing-packing materials.

10 Compositions I-X should be used for the manufacture of sealing construction materials, wherefrom compositions IV-VII can be also used for the production of inhibited films employed in corrosion-proofing and packing of metal articles.

15 Compositions XI-XIV with a high content of volatile inhibitors are advisable for the production of anticorrosion packing agents.

In contrast to the material according to the present invention, the anticorrosive material according to Japanese Patent No. 49-21223 can be used, on the basis of
20 its mechanical strength characteristics, as a corrosion-resistant packing agent, but not for the manufacture of construction sealing members and articles.

25 According to the data of the above Table 2, the rate of corrosion of a steel electrode contacting with a film of the anticorrosive material according to the present invention (compositions I-XIV) is by 12-50 times lesser than that for the anticorrosive material of Japanese Patent No. 49-21223.

30 The use of the anticorrosive material according to the present invention in sealing units of oil-and-gas equipment makes it possible to 1.5-2 times extend the period of exploitation of sealing assemblies of pump-compressor pipes, shafts and pistons of pumps due
35 to a reduced crevice corrosion and corrosive-mechanical

wear of a metal. An inhibited film produced from the anticorrosive material according to the present invention is advisable for corrosion-proofing of spare parts of machinery and equipment, as well as of mechanical-engineering tools by way of a sealed enveloping or thermovacuum moulding. An anticorrosion agent produced from the anticorrosive material according to the present invention and placed inside a sealed packing ensures protection of metal parts from corrosion even upon packing thereof into a non-inhibited film.

Therefore, the anticorrosive material according to the present invention features a high degree of protection of metal articles from corrosion due to an effective use of corrosion inhibitors, as well as a versatile application due to a broad range of physico-mechanical characteristics.

The anticorrosive material according to the present invention can be used for the manufacture of sealing structural members (gaskets, sealing rings and washers and the like), strippable anticorrosive coatings, as well as for the production of film materials and anticorrosive agents for packing purposes employed in corrosion-proofing and packing of metal articles.

CLAIMS

1. An anticorrosive material comprising polyethylene plasticized with a mineral oil and containing as an oil-soluble corrosion inhibitor:

(a) contact corrosion inhibitor selected from:

a sulphonated or nitrated mineral oil, or a product of neutralization of a sulphonated or a nitrated mineral oil with an alkali, or a product of neutralization of a sulphonated mineral oil with urea, or bottoms from distillation of synthetic or naturally occurring fatty acids, or products of condensation of said bottoms with organic amines, or a product of condensation of an alkenylsuccinic anhydride and urea, or

(b) a volatile corrosion inhibitor selected from:

a salt of dicyclohexylamine and an organic acid, or tertiary amine having a nitrile group; or

(c) a mixture of both contact (a) and volatile (b) corrosion inhibitors,

the proportions of the anticorrosive material components being as follows, per cent by weight:

mineral oil	20-45
oil-soluble corrosion inhibitor	2-50
polyethylene	the balance.

2. An anticorrosive material according to Claim 1, substantially as herein described in any of the foregoing Examples 1 to XIV of Table 1
